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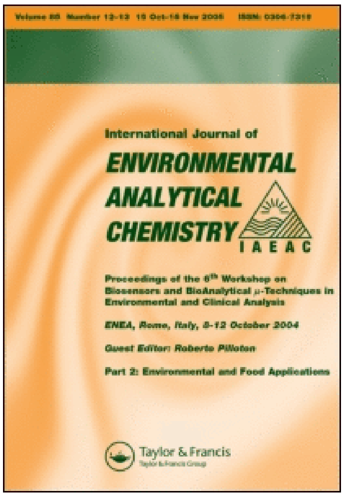

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Photodegradation of Diuron Induced by Iron(III) in the Aquatic Environment

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PHOTODEGRADATION OF DIURON INDUCED BY IRON(III) IN THE AQUATIC ENVIRONMENT

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The degradation of diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) photoinduced by iron(III) in aqueous solution has been investigated with different iron(III) species (monomeric species $Fe(OH)^{2+}$ and water soluble oligomeric species), in homogeneous phase under monochromatic excitation at 365 nm and under sunlight. The degradation of diuron was also studied in heterogeneous phase with a hydrated iron(III) oxide : $\alpha FeOOH$ (goethite). In homogeneous phase, the rate of degradation depends on the concentration in $Fe(OH)^{2+}$, the most reactive species in terms of $^{\bullet}OH$ radicals formation. The major photoproduct is 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea which represents more than 60% of diuron disappearance. The mechanism only involves the attack by $^{\bullet}OH$ radicals arising from iron(III) excited species. The half lives of diuron when submitted to such a process in the environment were estimated to be 1–2 hours and a few days according to the concentration of $Fe(OH)^{2+}$ (respectively 70% and <10% of total iron(III) concentration). In heterogeneous phase, the degradation of diuron is slower and the major photoproduct is 3-(3,4-dichlorophenyl)-1-methylurea.

Keywords: Iron(III); diuron; photodegradation; aqueous solution; goethite

INTRODUCTION

The contamination of aquatic bodies by harmful organic chemicals is one of the great environmental problems. Among the molecules used in agriculture, diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea, Figure 1) is widely used as a herbicide because of its inhibition of photosynthesis.

As a result it is found in water bodies [1,2]. Because its herbicidal activity is required during seed germination, diuron biodegradation has to be very slow and photochemistry with sunlight can provide an alternative way of degradation. In addition, it has been proven that the photodegradation of organic molecules in aqueous solution is accelerated by the presence of dissolved iron(III)

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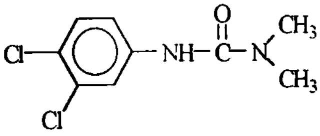


FIGURE 1 Structure of diuron

species [3,4]. This phenomenon is related, firstly to the fact that organic molecules do not significantly absorb solar light, whereas iron(III) in aqueous solution does absorb, and secondly that the photoredox process taking place upon excitation of iron(III) in aqueous solution gives rise to iron(II) and •OH radicals [5,6]. •OH radicals are known to be very active species for oxidizing most of organic substrates. The simultaneous reoxidation of iron(II) into iron(III) by oxygen confers a catalytic aspect to the process [7]. Hydrated iron(III) oxides are known to be dissolved in aqueous suspension by light with the release of iron(II) ion in the solution [8], the photodissolution being particularly efficient in the presence of organic ligands such as carboxylic acids [9,10]. This phenomenon is very important for the cycle of iron in natural systems and it usually reduces oxidized ligands which are then transformed [11].

BRIEF SURVEY ON COORDINATION COMPLEXES PHOTOCHEMISTRY

The absorption of a photon by a species A leads to the formation of a short-lived electronically excited state A*. The excess of energy can be dissipated physically or chemically. When the excitation takes place in a ligand to metal charge transfer transition (LMCT), it leads to an excited state in which the metal is reduced and the ligand is oxidized. The deactivation of such excited states can occur either by charge separation generating the reduced metal and the oxidized ligand in the ground state or by a physical process regenerating the starting material. The ligand after charge separation is of radical nature and is a highly reactive species. For instance aquo-complexes of iron(III) give rise upon irradiation and after charge separation to iron(II) and •OH radicals (cf later)

EXPERIMENTAL SECTION

The materials and the experimental conditions used in homogeneous phase were described elsewhere [12]. Concerning the work in heterogeneous phase:

Goethite (αFeOOH) was prepared according to Atkinson's procedure [13]. The solid was shown to be a pure phase: its IR spectrum and X-ray diffractogram were in agreement with the reported data [14,15].

The filtration of the aliquots of goethite aqueous suspensions was performed with Sartorius cartridge (Minisart RC 15, pore size 0.2 μm) before analysis.

The irradiation set up was a cylinder mirror made of stainless steel. The reactor, a water jacketed Pyrex tube, was located on its axis and three high-pressure mercury lamps (MAZDA MAW Type 125 W), the emission of which at 365 nm was selected by an inner filter (" black light "), were located around. The reaction medium was stirred. The absorbed light intensity measured by ferrioxalate actinometry was $I_a = 1.1 \times 10^{16}$ photons/sec/cm^3 for an irradiated volume of 50cm^3 [16].

Iron(III) monomeric species concentration was determined by complexometry with 8-hydroxyquinoline-5-sulfonic acid (HQSA). The absorbance of the resulting complex $Fe(HQS)_3$ was monitored at 572 nm as described by Faust. [5] The percentage of iron(III) monomeric species $Fe(OH)^{2+}$: $\%Fe(OH)^{2+} = \frac{[Fe(OH)^{2+}]}{[iron(III)]_{tot.}} \times 100$ was continuously decreasing in our experimental conditions : the decrease was fast at the beginning and slowed down with the ageing of the solution. Iron(II) concentration was determined by complexometry with *ortho*phenanthroline. Diuron degradation and photoproducts formation were followed by hplc (UV detection at 250 nm) by measuring the areas of the corresponding peaks.

RESULTS

Iron(III) and diuron in aqueous solution

Under our experimental conditions (c=0.20 mM and pH=3.35), iron(III) mainly exists as the monomeric species $Fe(OH)^{2+}$ [17], water molecules coordinating to iron(III) are omitted.

Diuron is only slightly soluble in water with a maximum of solubility of around c=0.18 mM [1]. A concentration of 0.05 mM was used for this work. The UV-visible spectrum of diuron in aqueous solution presents two absorption bands at $\lambda = 210$ nm ($\varepsilon = 21800\ M^{-1}\ cm^{-1}$) and $\lambda = 247$ nm ($\varepsilon = 13400\ M^{-1}cm^{-1}$) and a plateau at around 285 nm ($\varepsilon \approx 800\ M^{-1}cm^{-1}$). There is no more absorption at $\lambda > 310$ nm.

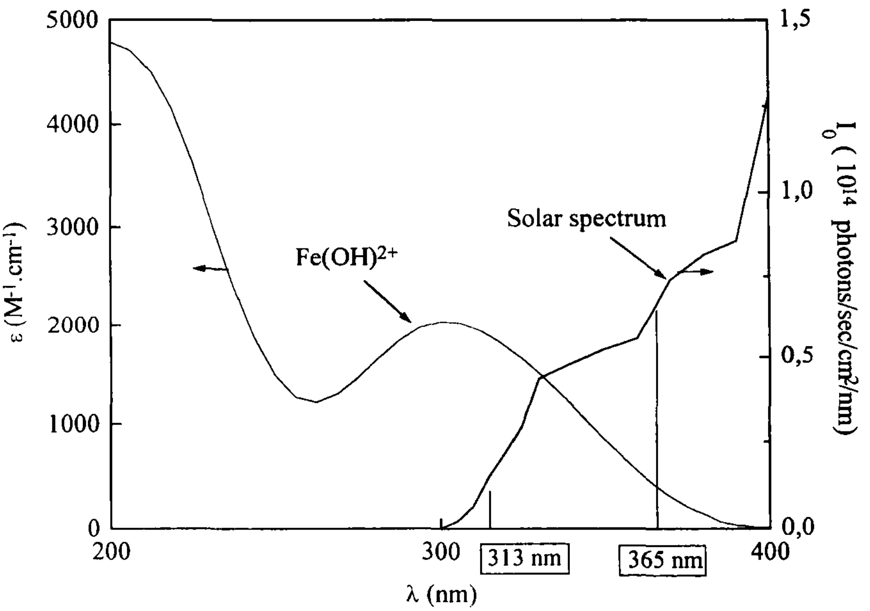


FIGURE 2 UV-visible spectrum of $Fe(OH)^{2+}$ and solar spectrum in June 1988

In Figure 2 is represented the UV-visible spectrum of $Fe(OH)^{2+}$ together with the solar light intensity [18,19]. When iron(III) (c=0.20 mM) and diuron (c=0.050 mM) were mixed together (pH=3.35: natural pH of the mixture), the resulting UV-visible spectrum was the sum of UV spectra of the components. There was no detectable complexation in the ground state. The solution was stable in the dark and there was neither redox reaction nor precipitation at least within a few days.

Photochemical behavior

Upon irradiation at λ>300nm, iron(III) species are known to undergo a redox process giving rise to iron(II) and $^{\bullet}OH$ radicals (reaction 1).

$$Fe(OH)^{2+} \xrightarrow[H_2O]{h\nu} Fe^{2+} + HO^{\bullet} \qquad (1)$$

The quantum yield that measures the efficiency of reaction(1) *i.e.* the efficiency of one photon to form iron(II) and $^{\bullet}OH$ radical, strongly depends on the excitation wavelength (Table I). The values of the quantum yield are also reported at two percentages of $Fe(OH)^{2+}$ at constant total iron(III) concentration.

TABLE I Photochemical features of aqueous iron(III) solutions:

Species	*Percentage (%)*	*ϕ Fe^{2+} form.*	*$\lambda_{exc.}$(nm)*
$Fe(OH)^{2+}$	100[a]	0.14	313
		0.017	360
$Fe(OH)^{2+}$	90[b]	0.08	313
		0.055	365
$Fe(OH)^{2+}$	11[b]	0.02	313
		0.008	365

[a] : ref 5
[b] : ref 12.

When the mixture was irradiated at 365 nm, a decrease in absorbance was observed all along the spectrum (Figure 3), iron(III) and diuron disappeared upon irradiation.

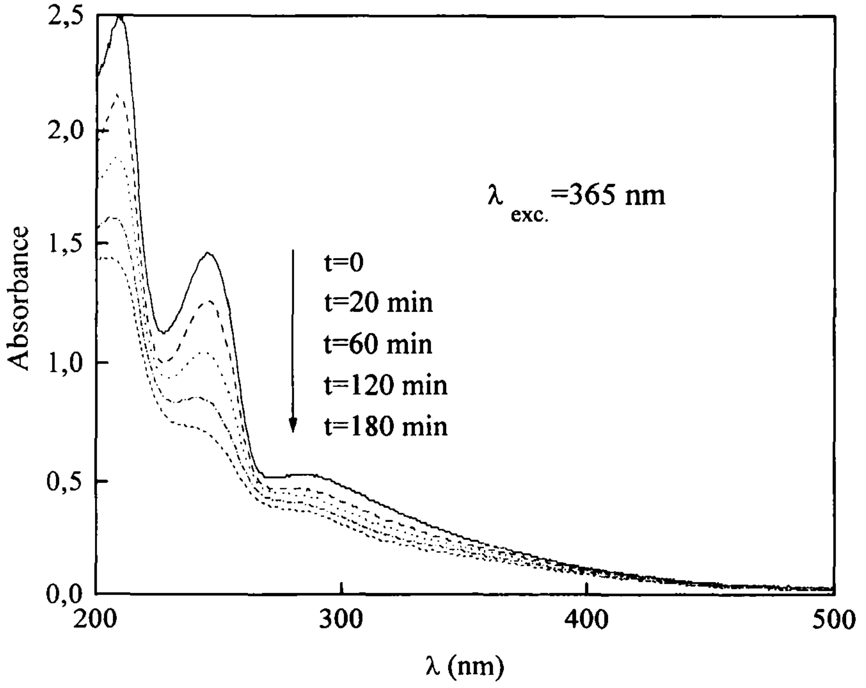


FIGURE 3 Spectral evolution of a mixture [iron(III)]=0.20 mM with 70% of $Fe(OH)^{2+}$ [diuron] = 0.050 mM upon irradiation at 365 nm

In Figure 4 is represented the diuron disappearance upon irradiation of an iron(III)-diuron mixture containing different perçentages in monomer $Fe(OH)^{2+}$ 70% – 50% and less than 5% for a constant total concentration in iron(III) in the solution (0.20 mM). The rate of diuron degradation was divided by a factor of about 100 when the percentage of monomer went down from 70 % to a value lower than 5 %. The kinetics of diuron disappearance appeared to be of first order whatever the percentage of $Fe(OH)^{2+}$ in the iron(III) solution.

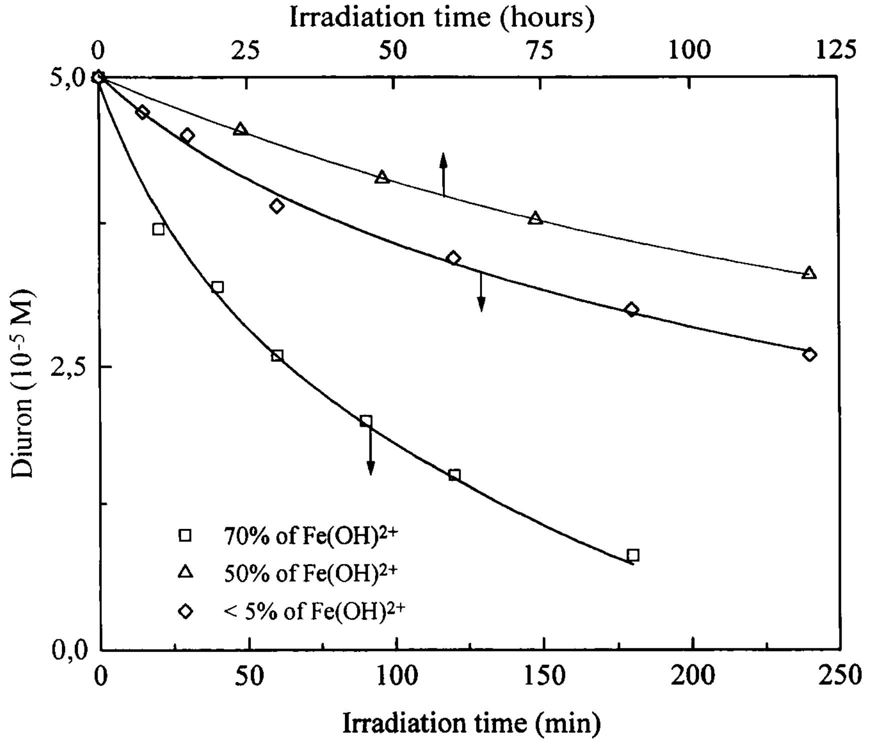


FIGURE 4 Kinetics of diuron disappearance upon irradiation at 365 nm with different percentages of monomeric species in the iron(III) solution

The rate constants are gathered in Table II. In order to be able to compare the apparent effiency of the photons for the different percentages, a pseudo value of quantum yield of diuron disappearance was also calculated by dividing the rate of disappearance by the number of photons absorbed by the solution per second (Table III). The formation of iron(II) was also strongly affected by the percentage of $Fe(OH)^{2+}$ (Figure 5). The quantum yield of iron(II) formation was not significantly affected by the presence of diuron. The pseudo quantum yields of diuron disappearance "ϕ" were also measured upon irradiation at 313 nm again with two different percentages of monomeric form (Table III). In all cases, the complete degradation of diuron was observed.

TABLE II First order apparent rate constants for diuron degradation

% $Fe(OH)^{2+}$	*$k_{app.}$ (min^{-1})*
70 %	96×10^{-4}
50 %	25×10^{-4}
< 5%	0.66×10^{-4}

TABLE III Quantum yields upon excitation at different wavelengths

	% monomer $Fe(OH)^{2+}$	*70 %*	*50 %*	*< 5 %*
$\lambda_{exc.}$ = 365 nm	ϕ Fe^{2+} form.	2.6×10^{-2}	1.0×10^{-2}	1.3×10^{-4}
	"ϕ" diuron dis.	6.5×10^{-3}	1.0×10^{-3}	2.5×10^{-5}
$\lambda_{exc.}$ = 313 nm	"ϕ" diuron dis.	5.0×10^{-2}	-	1.6×10^{-4}

In the absence of oxygen and upon irradiation at 365 nm, the formation of iron(II) was slowed down by a factor of 2 but the disappearance of diuron was almost completely inhibited, the degradation was only detectable by the presence of traces of hydroxylated photoproducts.

When irradiated at 365 nm in the presence of isopropanol used as a scavenger of $^{\bullet}OH$ radicals, there was no degradation of diuron whereas a significant formation of iron(II) was observed.

Identification of the photoproducts

Several peaks appeared in the HPLC chromatogram of an irradiated mixture (Figure 6). The main photoproducts were identified (cf scheme 1). The hydroxylation products of the aromatic ring **1** and **2** were detected near the injection peak. These two compounds have been already observed by Tanaka et al. [20] who investigated the direct photolysis of diuron under ultraviolet excitation.

The major photoproduct **3** and photoproduct **4** were identified respectively as 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea and as 3-(3,4-dichlorophenyl)-1-methyl urea by comparison with authentic samples synthesized by analogy with

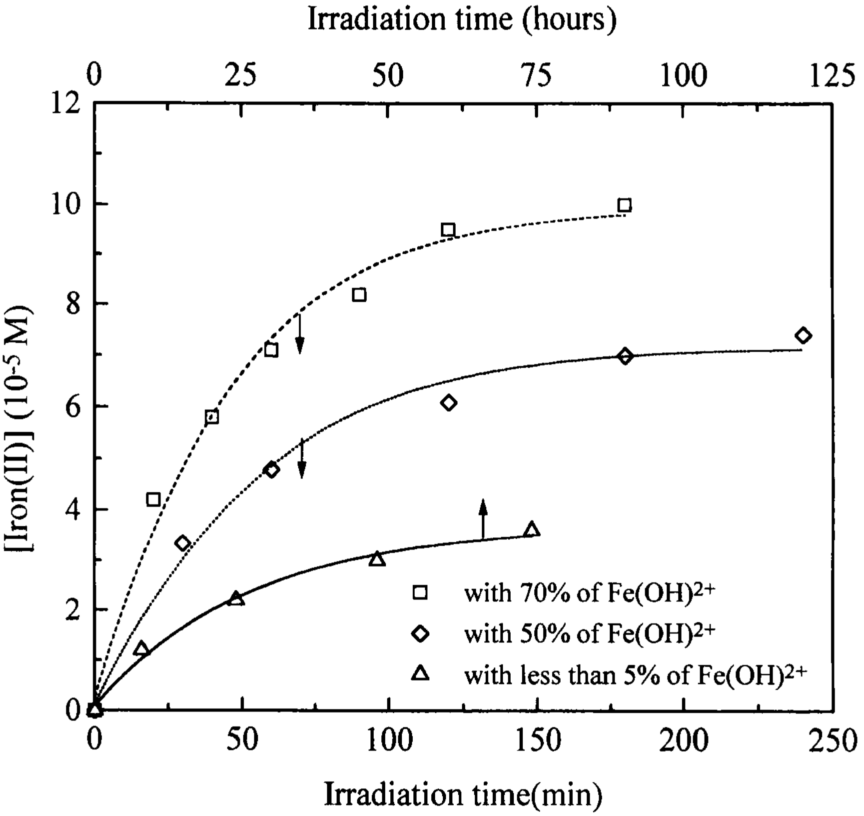


FIGURE 5 Kinetics of iron(II) formation upon irradiation at 365 nm with different percentages of monomeric species in the iron(III) solution

Crosby's procedure [21]. The secondary photoproducts **5** and **6** were isolated and identified by mass spectrometry [22] each of them accounts for about 5% of diuron disappearance.

The mass balance of diuron disappearance was around 75 % if we only considered photoproducts **3**, **4** and **5**. We were not able to quantify the formation of the hydroxylated products. However the overall mass balance of diuron degradation seemed to be near 90%.

Degradation of diuron in goethite aqueous suspensions

The conditions for the study were the following :

[Diuron]=0.01 mM, pH=7.2, the mass of goethite was varried between 0.20 and 0.70 g/L.

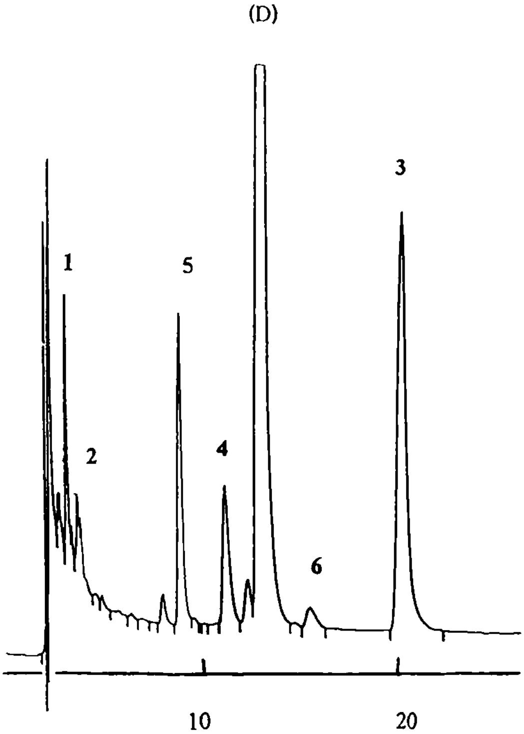


FIGURE 6 HPLC chromatogram of a mixture [iron(III)]=0.20 mM with 70% of $Fe(OH)^{2+}$ [diuron] = 0.050 mM irradiated 90 minutes at 365 nm. (D) : diuron, **1...6** : photoproducts Detection : λ = 250 nm, Eluant : MeOH : 60%,H_2O : 40%, 0.1% H_3PO_4

There was no detectable adsorption of diuron at the surface. When such suspensions were irradiated at 365 nm, we observed a slow degradation of diuron and the formation of the products **3** to **6**. The formation of iron(II) could not be detected and the UV-Visible spectra of the aliquots after filtration did not show any traces of iron(III) aquo-complexes. The only photoproduct which accumulated in the suspension is 3-(3,4-dichlorophenyl)-1-methylurea (**4**), the others (**3**,**5** and **6**) were present but their concentration were almost stable. The disappearance of diuron when a mixture ([Diuron]=1.0 × 10^{-5} mol/L and goethite 0.4g/L) was irradiated at 365 nm is presented in Figure 7 together with the formation of the product **4**. This product only represented 20% of diuron disappearance. The initiale rate of diuron disappearance increased by a factor of 1.5 when the mass of goethite went up from 0.20 to 0.70 g/L.

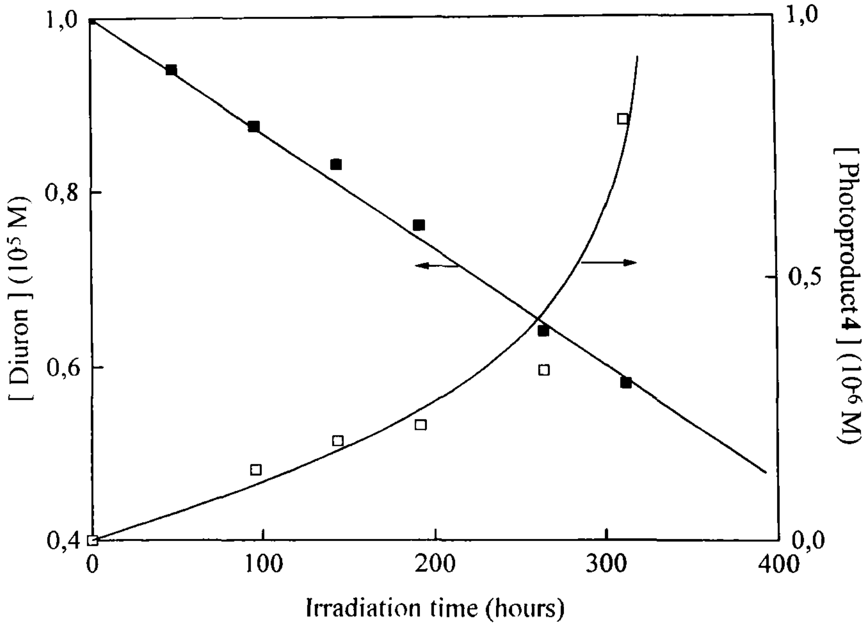


FIGURE 7 Kinetics of diuron disappearance and photoproduct 4 formation upon irradiation at 365 nm of a goethite aqueous suspension (goethite: 0.40 g/L, [diuron]=0.010 mM)

Irradiation under solar light in homogeneous phase and projection to environment

A mixture of diuron (0.050 mM) and iron(III) (0.20 mM, 70% of monomeric form $Fe(OH)^{2+}$) was exposed to solar light during a sunny day in July. After two hours, 90 % of the diuron had disappeared, and the photoproducts were analogous in nature and percentage to those observed upon excitation at 365 nm. The only difference was the presence of a small amount of dichloroaniline, a product never observed at 365 nm. After 5 hours, no more photoproduct was detectable by hplc (UV detection, λ=210 nm) : the degradation of diuron and of the aromatic photoproducts was complete.

With an iron(III) solution containing less than 10 % of $Fe(OH)^{2+}$, the rate of diuron degradation strongly decreased but the reaction was complete after 70 hours.

The life time of diuron when it undergoes the attack of $^{\bullet}OH$ radicals coming from excitation of iron(III) aqueous solution was estimated as described by ECETOC [23]. It is based on the experimentally determined "quantum yield" of diuron disappearance, on the absorption spectrum of iron(III) and on the solar irradiation intensities.

The half life $\tau½$ is defined as :

$$\tau_{1/2} = \frac{\ln 2}{2300 \int_{\lambda_1}^{\lambda_2} \phi(\lambda).I_0(\lambda).\varepsilon(\lambda).d\lambda}$$

where

$\tau½$ = half life in s

ϕ= the "quantum yield" of disappearance of diuron in molecule.photon^{-1} or mol.einstein^{-1} at λ in the range λ_1-λ_2

I_0 = intensity of sunlight at wavelength λ in einstein cm^{-2} s^{-1} nm^{-1}

ε = molar extinction coefficient at wavelength λ in M^{-1} cm^{-1}

2300 = a factor taking into account the conversion of liter into cm^3 and of decadic units into Naperian logarithms.

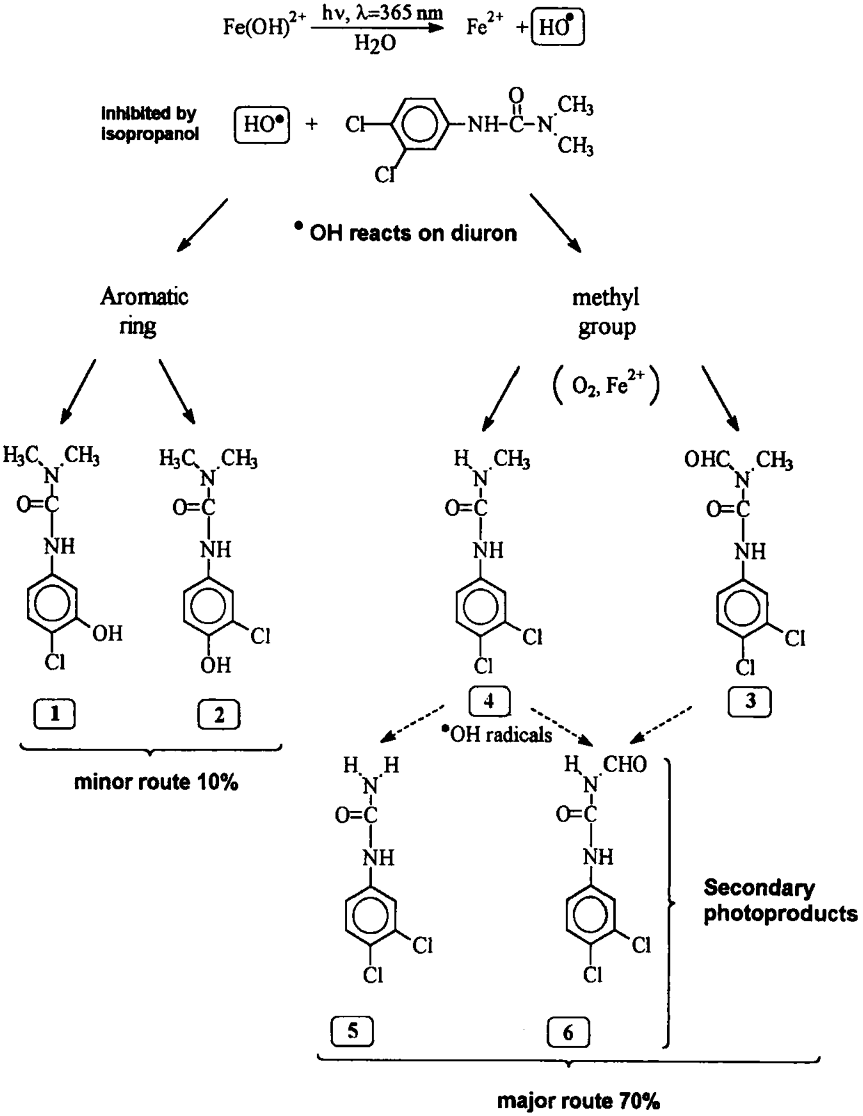
The half lives were calculated using the solar irradiation intensities as presented in the literature [19]. The half lives were estimated to be around 1–2 hours and a few days for solutions containing 70% and less than 10% of monomeric form $Fe(OH)^{2+}$respectively. These estimations are in good agreement with our results obtained upon irradiation by solar light in this work.

DISCUSSION

Iron(III) species are the only absorbing species when a mixture of diuron and iron(III) in aqueous solution was irradiated at 365 nm. Iron(III) aqueous species are known to undergo a redox reaction giving rise to iron(II) and $^{\bullet}OH$ radicals, according to equation (1). Among the iron(III) species present in the solution, $Fe(OH)^{2+}$ the monomeric form present under our experimental conditions (pH=3.35) is the most photoreactive one. Accordingly, the rate of diuron photodegradation strongly depends on $Fe(OH)^{2+}$ concentration at constant iron(III) total concentration. In terms of diuron degradation, the mechanism only involves the attack by $^{\bullet}OH$ radicals as evidenced by the total inhibition observed when 2 % of isopropanol is added to the solution. The rate of diuron degradation is strongly affected by the excitation wavelength. It increases when $\lambda_{exc.}$ comes down from 365 nm to 313 nm. It is in agreement with the notion that ejection of $^{\bullet}OH$ radical from the solvent cage requires kinetic energy [6].

The nature of the photoproducts and more particularly the nature of the major one **3**, shows that the attack of $^{\bullet}OH$ radicals is mainly on the methyl group, it is also true for the photoproduct **4** and even for the secondary photoproducts **5** and

6. The formation of hydroxylated products (attack on the benzene ring) only represents a minor route accounting for a few percent of diuron degradation. From the experimental results, the degradation of diuron photoinduced by iron(III) can be represented as in scheme 1.



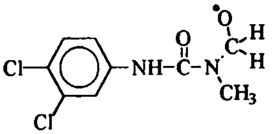
SCHEME 1

As already mentioned, the first step is the absorption of the light by iron(III) species leading to the formation of $^{\bullet}$OH radicals. Then two different sites of attack on the molecule are possible :

- $^{\bullet}$OH radicals react with the aromatic ring to form an adduct with the subsequent loss of a chlorine atom and the formation of hydroxylated photoproducts **1** and **2**. This route only represents a minor way of diuron degradation.
- $^{\bullet}$OH radicals attack the methyl of the dimethylurea group. The alkyl radical $R^{\bullet}$ reacts with oxygen to form $RO_2^{\bullet}$ leading to the formation of a hydroperoxide. The subsequent hydroperoxide decomposition occurs by a Fenton type reaction with iron(II) giving rise to the alcoxyle radical [24].

$$ROOH + Fe^{2+} \xrightarrow{H_2O} RO^{\bullet} + Fe^{3+} + HO^{-}$$

Where RO$^{\bullet}$ is



Photoproducts **3** and **4** result from the classical β-scissions of RO$^{\bullet}$ [25].

Secondary photoproducts **5** and **6** are rapidly observed . Their formation is possible by a second attack of HO$^{\bullet}$ radicals on the photoproducts **3** or **4**. This accounts for the formation of photoproduct **4** in low yield (less than 5%).

In heterogeneous phase, there was no detectable adsorption of diuron at the goethite surface. In the absence of any iron species in the irradiated solution, the phenomenon of diuron degradation may be due to a photocatalytic effect of the goethite (it means that upon irradiation, there is formation of free electrons and positives holes at the solide surface, the latter generating HO$^{\bullet}$ radicals).

CONCLUSION

The degradation of diuron photoinduced by iron(III) only involves the attack by $^{\bullet}$OH radicals arising from iron(III) species in the excited states. The percentage of monomeric iron(III) species, $Fe(OH)^{2+}$, appears to be the parameter controlling the rate of diuron degradation : the higher the percentage, the faster the degradation is. The degradation photoinduced by iron(III) can represent a very efficient way for elimination of diuron. The degradation of diuron in an aqueous suspension of goethite eventhough the process is slower than that observed in homogeneous phase cannot be ignored in the aquatic environment.

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